PRODUCTION OF MAGNESIUM BY THE ELECTROLYSIS OF FUSED SALTS

BY

A. N. GROSSMAN

ARMOUR INSTITUTE OF TECHNOLOGY

1915

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The production of magnesium
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THE PRODUCTION OF MAGNESIUM

BY THE

ELECTROLYSIS OF THE FUSED SALTS

A THESIS

Presented by

Alexander N. Grossman

to the

President and Faculty

of

Armour Institute of Technology

For The Degree Of

Bachelor of Science In

Chemical Engineering

Having completed the prescribed course

of study in Chemical Engineering

1915

Approved.

H.M. Raymond

Dean of Engineering Studies.

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Professor of

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L. C. Monin

Dean of Cultural Studies.

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Introduction

The great lack of really practical information and knowledge about nearly all industrially successful processes in electro-chemistry outside of that possessed by those practising the various branches of the industry is due to our commercial conditions which make it necessary for the producers to jealously guard their secrets from competitors, to the great detriment of the advance ofthe science and industries as a whole. In such a situation, there are necessarily very few people possessing an extensive practical knowledge on a particular subject who are likely to write about it.

The author has undertaken the study of the real conditions which must be adhered to in order that the electrolysis of the fused salt, magnesium chloride come to a successful culmination for the production of the metal Magnesium.

These conditions are;

(a). The type of crucible.

(b). The type of electrodes to be used so that they will not be attacked

by the electrolyte or the gases given off in the reaction.

(c). The current density.

(d). The temperature.

(e). The specific gravity of the electrolyte.

(f). The removal of the products of the electrolysis.

There are certain details of the process which have been studied by such men as Oettal and are of interest since they show the difficulties which one meets, not obvious from a consideration of the true principles of the process, but very prominent when put to an actual performance and test.

The author desires to thank Prof. H. Mac Cormack for his many suggestions, Prof. B.B. Pulsifer, under whom this work was carried on, and Prof. E. Freeman of the Electrical Department, for the loan of and recharging of the ten Edison storage cells used in this work.

Alexander N. Grossman.

May 27, 1915.

Armour Institute of Technology.

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The Water Jacketed Cell...........Figure Six

The Fischer Cell....................Figure Seven

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BIBLIOGRAPHY

"Annalen" 82--137

The first work of Bunsen is described for the successful winning of the metal from the fused electrolyte.

Edgar A. Aschcroft.
"Electro-Chemical and Metallurgical Industry"
Volume 4, Page 143. April 1906.
" Factory Scale Experiments with the Fused Electrolytes".

An article on the fused electrolytes as applied to zinc chloride electrolysis. There is no doubt many suggestions in this article which could be carried out in the work on magnesium chloride should this salt be electrolyzed on a large or factory scale.

G. Taborvsky.
Zeitschrift fur Elektrochemie, July 28,1906.
" Magnesium Anodes "

In neutral solutions of chlorides and sulphates, hydrogen is developed at the magnesium anodes and

a black powder goes into solution, known as Beetz Suboxide, which is in reality magnesium. He finds that the potential at which this takes place is the same as metallic magnesium when no current flows.

Bertram Blount
" Practical Electro-Chemistry " 1901
The book contains an entire chapter on the production of magnesium. He gives a description of the process, speaks of the difficulties one meets with in this work, gives some theory, some of the uses and is as thorough as one can be on a subject on which very little has been written.

Dr. W. Borchers.
" Electric Smelting and Refining " 1904

Dr. Borchers has written the best account of magnesium as produced by the electrolysis of its chloride. He gives a brief history of the process, tells of the cell which he has patented for this

work and gives some of the difficulties of the process. Mr. Borchers himself has done a large amount of work with fused salt as the electrolyte and his work may be considered as authoritative on the subject.

Caron and Deville.
Ann. Chim. Phys. 1863 67 347

Metallic sodium was allowed to react with magnesium chloride and calcium fluoride. The resulting metal was distilled in an iron crucible, covered so that the air supply is cut off and the little air that remains in the cell is replaced with hydrogen or any coal gas free from oxygen.

Dr. Heinrich Danneel.
" Electro-chemistry " 1907

A book on theoretical electro-chemistry and its physico-chemical foundations.

THE PRODUCTION OF MAGNESIUM BY ELECTROLYSIS

Henry C. Jones.

" Outlines in Electro-Chemistry"

A book on the theoretical side of the subject of electrolysis. He deals with the theory of electrolysis, electrolytic dissociation, its applications and methods of calculations.

J. C. Matthiessen

" A Fused Salt Electrolyte for Magnesium "

Journal American Chemical Society 1856 8 107

He describes the electrolysis of the fused salt for the metallic magnesium and believes that the addition of potassium chloride will aid materially in the electrolysis.

John B.B. Kershaw.

" Electro- Metallurgy" 1908

An outlook into the metallurgical industry where the electric current is the means of extraction of the metal from the fused salt. He recommends the use of the Haag Cell for the electrolysis of magnesium chloride. A short description is as follows; The cell is divided

into three sections. The upper one receives the raw material and it is melted here by resistance heat. The central section is the electrolyzing chamber. Perforated carbon plates are the electrodes. The lower section of the cell will contain the molten magnesium as well as some of the undecomposed carnallite. By an ingenious device they are discharged separately. Chlorine rises in the hollow and perforated anode and passes the funnel shaped hood which covers the upper section of the cell. Liquid seals keep all parts gas tight and the fused salt is generally used for this purpose. Heat losses are avoided by placing the cell in an air chamber.

Dr. Robert Lupke
" The Elements of Electro-Chemistry " 1903

Dr. Lupke goes into the subject of general electro-chemistry, giving examples of the various types of experiments. Under magnesium, he gives the clay pipe experiment of Bunsen as an example.

THE PRODUCTION OF MAGNESIUM BY ELECTROLYSIS.

M. Mabrovsky

Zeitschrift fur Elektrochemie. 1905.11.465.

He finds that magnesium will combine with the oxides of other metals to form that metal itself. This is due to the great reducing power of the magnesium. It is now used to make silicon and boron.

Henry Moissan

" Traite De Chimie Minerale " Vol. 3 1906

He goes into detail regarding magnesium. He treats with its history, the method of manufacture, applications to the industry, its physical and chemical properties as well as the various salts which it forms.

Dr. Felix Oettal.

" Exercises in Electro-Chemistry " 1897

A good laboratory book giving the method for the electrolysis of the chloride, and explains the precautions which must be adhered to in to win the metal from the salt.

THE PRODUCTION OF MAGNESIUM BY ELECTROLYSIS.

Dr. Erich Muller

" Electro-chemisches Praktikum "   1913

An excellent work on the subject. He spends four pages on magnesium, recommending the use of a graphite crucible with a sheet iron cover and that fluorspar be added as a fluxing material. He claims that the efficiency of the process is between 50-58% of the total current supplied.

Dr. Felix Oettal

Zeitschrift fur Elektochemie. Vol.2 Page 394 1895

He shows that the presence of magnesium sulphate is detrimental to the electrolysis of the salt.

H. E. Roscoe and C. Schorlimmer

" A Treatise on Chemistry   vol. 2 The Metals.

He describes the preparation, properties and many of the salts which the metal forms. He recommends that fifteen hundreths ampere per square cemtimeter of cathode area be useda as the current density.

THE PRODUCTION OF MAGNESIUM BY ELECTROLYSIS.

Erwin S. Sperry

The Brass World Vol. 2 1907

He adds two ounces of metallic magnesium to one hundred pounds of copper for fine sand casting. He claims it is better than silicon used in this work heretofore, that it does not impair the conductivity, that it is a good absorber of carbon monoxide gas, and that it aids in the elimination of the blowholes. The carbon monoxide reacts with the magnesium to form magnesium oxide and carbon.

Tucker and Jouard

Transactions American Electro-Chemical Society

Volume 17, 1910.

They give the results of the wotk done at Columbia University which show good work and an efficiency of about forty five per cent for the process.

THE PRODUCTION OF MAGNESIUM BY ELECTROLYSIS.

E. R. Frary

Transactions American Electro-Chemical Society

Not published as yet. Read at Annual meeting 1915

" The Presence of The Suboxide of Magnesium "

He proves the presence of the suboxide as a detriment to the electrolysis.

Dr. Herman von Fehling.

" Neues Handwurterbuch der Chemie " 1886

Vierter Band

A two page discussion on magnesium,its properties, method of manufacture and a few of its uses. An old book, but still quite thorough.

F. G. Wiechman

" Notes on Electro-Chemistry " 1906

A book on general electro-chemistry. He gives a short review of the conditions whichmmust be adhered to for successful work.

THE PRODUCTION OF MAGNESIUM BY ELECTROLYSIS

A. Winkler.

" Berichte der Deutchen Chemische "   Vol. 24 Page 873

He discusses the reduction of the oxygen compounds by the aid of magnesium. The work is similar to that of Baborvsky.

The Hemelinger Aluminum and Magnesium Works.

" The Preliminary Preparation of the Charge for the Electrolysis of Fused Magnesium Chloride ".

German Patent # 115015

Having carnallite at hand, it is fused without purification with magnesium chloride,sodium or potassium chloride or dehydrated artificial carnallite to bring it to the following composition;

Magnesium chloride.......	41.66%
Potassium chloride	32.66%
Sodium Chloride	25.66%

This gives a salt with the formula as

$MgCl_2.KCl.NaCl.$

A little fluorspar is added to make the metal flow easily.

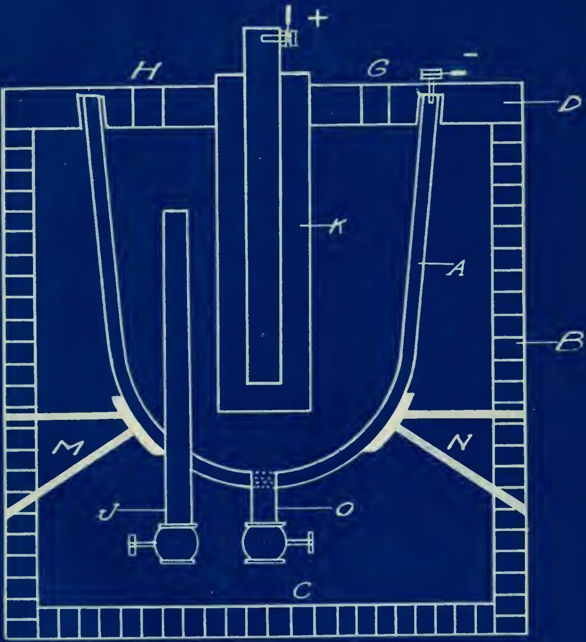

Figure 1

THE PRODUCTION OF MAGNESIUM BY ELECTROLYSIS.

E. L. Roberts

United States Patent # 778270 issued Dec. 27, 1904

" An Electrolytic Cell "

Figure one is a diagram of the apparatus illustrating the patent where an iron pot "A" is placed in a furnace "B" of some refractory material and heated on the outside by the fire "C". The pot is covered with a slate cover "D" with a hole in it for the anode rod. The vessel itself will act as the cathode. "H" is the feed guide hole and entrance for the inert gases. "G" carries off the gases. There is a drawoff at "O" and "J" so that the same vessel may be used for both low and high specific gravity work. A porcelain tube "K" protects the magnesium from the anode, the source of the liberation of the chlorine. No information is given as to the electromotive force at which the cell is operated. "M" and "N" are two steel stays set in the brick to hold the crucible in the furnace. He gives the following formula for use

in the electrolysis:

Lithium Fluoride	120 parts
Potassium Chloride	80 parts
Magnesium Oxide	20 parts
Sodium Chloride	40 parts
Ammonium Chloride	20 parts
Magnesium Chloride	10 parts
Magnesium Fluoride	80 parts

Chloribe is liberated at the anode along with oxygen. The lithium lowers the specific gravity of the bath as well as the fusion point. Magnesium oxide raises the specific gravity of the bath and is recommended for high level work.

E. A. Touceda.

" Anti-Friction Alloy "

United States Patent # 933139 issued Sept. 7, 1909

He makes an alloy of magnesium, cadmium and lead. The purpose of the magnesium is to increase the hardness and to brighten the alloy. The analysis:

Magnesium	0.10% -5.00%
Cadmium	10.00%
Lead	85%- 89.90 %

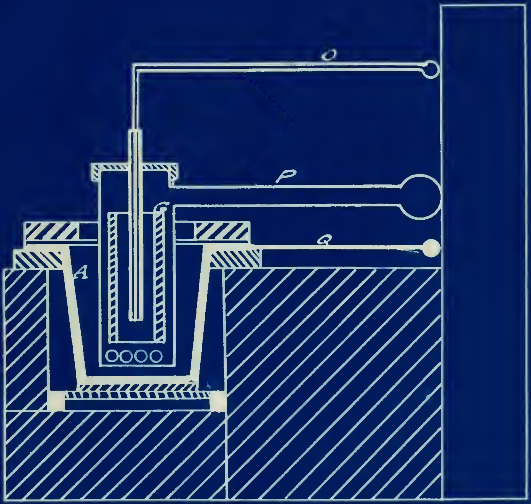

Figure 2

THE PRODUCTION OF MAGNESIUM BY ELECTROLYSIS.

Heinrich Graetzel

" An Electrolytic Cell"

German Patent #26962

This is in reality a combination of several ideas. The improvement in the apparatus for the production of magnesium is the use of a melting vessel as a cathode and the final separation of the electrolyte. The method also improves and gives a more complete separation of the chlorine which is liberated at the anode. The melting vessel "A" is of cast steel resting on magnesite brick, below which the heat is brought in through several flues. A carbon electrode is suspended in the vessel "G" and is surrounded by a porous cup. The vessel "G" is made of either fire clay, porcelain or any non-conducting material. It is perforated at the side and bottom. Reducing gases are led into the cell through "O" and taken out at "Q", this being also a terminal of the cathode. Chlorine is taken off at "P". All magnesium which is formed goes to the bottom. The real patent is

for the magnesium-carbon plate which is added when the bath becomes weak and the resistance so high that very little current travels through. These plates are placed parallel to the carbon electrode. The carbon will combine with the oxggen while the metal will combine with the chlorine and by forming magnesium chloride concentrate the solution. The method failed in its operation. The apparatus is shown in Figure Two.

M. Ruthenberg
" An Anode for Chloride Electrolysis"
United States Patent # 882169 Issued March 17, 1908
Review in Electro-Chemical and Metallurgical Industry.

He makes an electrode from a compound of silicon and another substance, a conductor of electricity as carbon, copper or any substance which can withstand the action of chlorous acid. The alloy should contain 10-25% of silicon.

THE PRODUCTION OF MAGNESIUM BY ELECTROLYSIS

G.O. Seward and F. von Kugelchen
United States Patent # 865648 issued Sept. 10, 1907
Review, Electro-Chemical and Metallurgical Industry
Volume Four, October 1907

This is the first of a chain of patents which have been issued to these men for the production of magnesium. In this particular patent, they aim to obtain an alloy of magnesium and calcium. The theory is that a metal should be selected that is less electro-positive, having a higher decomposition voltage than the more electro-positive compound, so that secondary reactions take place only to the extent that will be necessary for the formation of the alloy.

G. O. Seward and F. von Kugelchen
United States Patent # 868226 issued Oct. 15, 1907
Review, Electro-Chemical and Metallurgical Industry
Volume Four, November 1907

The electrolyte is magnesium chloride and potassium chloride. The object of the patent

is to add six per-cent of fluorspar to increase the specific gravity of the electrolyte and as a result float the metallic magnesium. Barium fluoride may also be used as a substitute.

G. O. Seward and F. von Kugelchen
United States Patent #880489 issued Feb. 25, 1908
Review, Electro-Chemical and Metallurgical Industry
Volume Five, April 1908

The electrolyte in this case is the oxide of magnesium in a fused mixture of magnesium fluoride and one or more alkaline fluorides or alkaline earths. The proportions are as follows;

Magnesium fluoride.......2 parts
Lithium fluoride.........1 part
Calcium fluoride.........1 part

The magnesium fluoride has a lower decomposition voltage than the other fluorides and therefore is decomposed first within certain limits. Magnesium oxy-chloride may be substituted for the fluoride salt. Oxygen and chlorine are evolved at the anode.

THE PRODUCTION OF MAGNESIUM BY ELECTROLYSIS

As the magnesium salt is exhausted, a new supply is added constantly to keep the bath saturated.

G. O. Seward and F. von Kugelchen
United States Patent # 881934 issued Mar. 27, 1908
Review, Electro-Chemical and Metallurgical Industry
Volume Five, May 1908

Magnesium oxide, magnesium fluoride and lithium fluoride are fused and used as the electrolyte. The cathode is molten aluminum. The magnesium oxide is fed in contimously. Instead of the oxide of magnesium being dissolved in the fluoride bath, aluminum oxide and magnesium oxide may be dissolved in the bath and an alloy of magnesium and aluminum set free at the cathode. Magnesium oxychloride may be used to replace the oxide.

G. O. Seward and F. von Kugelchen
United States Patent # 900961 issued Oct. 13, 1908
Review, Electro-Chemical and Metallurgical Industry
Volume Five November 1908

Magnesium fluoride and calcium chloride are

fused to drive off the water of crystallization and then an alkaline fluoride is added as a flux. The magnesium will collect at the cathode while the calcium chloride will be converted to the fluoride state. When the electrolyte becomes exhausted, it is mixed with fused hydrated magnesium chloride and heated. The reaction:

$$MgCl_2 + CaF_2 \rightarrow MgF_2 + CaCl_2$$

G. O. Seward and F. von Kugelchen
United States Patent # 931392 issued Aug. 17, 1909
Review, Electro-Chemical and Metallurgical Industry
Volume Six, October 1909

It is only certain conditions that the electrolyte will be lighter than the metal magnesium and this is only regulated by a regulation of the temperature. In this manner the process is exceedingly difficult to manage. They propose to add barium chloride to replace the potassium chloride which is now used to a great extent.

They propose the following bath:

Magnesium chloride	5 parts
Potassium chloride	5 parts
Barium chloride	35 parts

The entire mass is fused and then electrolyzed. They claim that the metal will float very readily on top of the bath.

G. O. Seward and F. von Kugelchen
United States Patent # 935796 issued Oct. 5, 1909
Review, Electro-Chemical and Metallurgical Industry
Volume Six, November 1909

The process which they desire to carry out takes place in two distinct operations. First, they produce an alloy of magnesium with a metal less electro-positive as aluminum by the electrolysis of the molten material with an insoluble anode and a cathode of a less electro-positive metal as aluminum. Then, second, there will be a consecutive dissociation, dissolution and deposition from the alloy, the latter being used

THE PRODUCTION OF MAGNESIUM BY ELECTROLYSIS.

as the anode in a suitable electrolyte. In this way, a pure magnesium is obtainable.

In the first step, a low specific gravity electrolyte is used and the material will sink to the bottom. In the second step, a high specific gravity electrolyte is employed to insure the flotation of the magnesium. Molten aluminum forms at the cathode in the first step and an alloy of magnesium and aluminum at the anode in the second step.

The electrolyte in the first step is magnesium chloride and potassium chloride. A carbon anode and aluminum cathode are used. When the alloy of magnesium and aluminum becomes rich, (50%-60%), it is removed either in part or whole and used as the anode for the second step.

The electrolyte in the second step may be the same as in the first step, with the addition of a heavier salt of the more electro-positive metal than magnesium is added.

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Barium chloride is adapted for this purpose. Magnesium alone is dissolved and re-deposited, care being taken not to exhaust the anode too much for its magnesium content. A large part of magnesium formed at the cathode in the second step is removed from time to time and most of the nearly exhausted material is then tapped off and replaced with a saturated electrolyte.

PH YSICAL AND CHEMICAL PROPERTIES OF MAGNESIUM.

When pure, magnesium is a silvery white and lustrous metal, melting at 650°C. and boiling at 1000°C. Its fracture shows a granular but crystalline structure. It is malleable, ductile and has but little tenacity. It can be rolled and pressed into wire and ribbon. It is quite susceptible to polishing. Its specific gravity is 1.75, its conductivity is 25.47 at 25°C. basing our calculation on silver equivalent to 100, and is the highest in the list of metals based on the electro-positive solution pressure. Its critical voltage is 3.26 volts/

Magnesium remains stable in the dry atmosphere, but in moist air, it readily assumes a film of the oxide. It burns with a white and very intense flame, giving violet and ultra-violet rays as is shown by the spectroscopic analysis. Its heat of combustion is 143,400 calories per gram. It not only forms the oxide when burned in air, but also

the nitride. The metal when heated will decompose steam, evolving hydrogen and the magnesium being changed to magnesium oxide. It also burns in carbon dioxide gas with the deposition of carbon. It dissolves in dilute acids and will decompose concentrated sulphuric acid at 215°C.

Magnesium has been prepared by the electrical method in the form of an olive green unstable colloidal solution in ether. Magnesium can liberate not only other metals but also the metalloids, for example, carbon dioxide, carbon monoxide and boron trioxide.

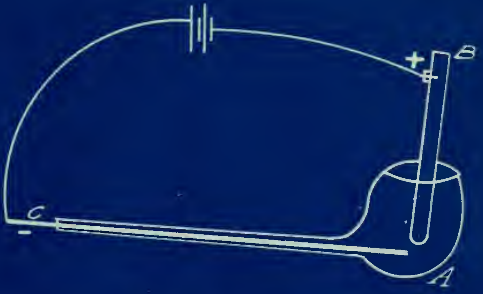

Figure 3

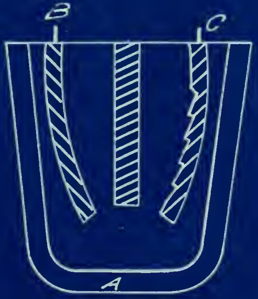

Figure 4

APPARATUS AND METHODS

The first real work on magnesium was done by Sir Humphrey Davy in 1780. He attempted to obtain the metal by the electrolysis of magnesium oxide and also by the action of potassium on the oxide which had been heated to a white heat. He was unsuccessful, however, in his attempts. Bussey did similar work in 1829 along with Wohler, but the metal could not be won.

In 1852, Bunsen, the great chemist and physicist, successfuly isolated the metal from the fused salt, magnesium chloride. His first apparatus is shown in Figure Three. A clay pipe "A" tilted so that none of the fused salt would leak through the stem of the pipe was used for this work. A carbon rod "B" was dipped into the bowl of the pipe and acted as the anode. A large iron or steel knitting kneedle "C" was inserted through the stem and acted as the cathode. The current was sent through the electrolyte and after a time when the material was broken up, small

globules of metallic magnesium were found. He found that the metal was attached to the cathode and the gas chlorine was liberated at the anode. He also found that the action of the chlorine itself was so great that if the chlorine came in contact with the metal at that temperature, the salt, magnesium chloride was formed again.

He then designed a cell as shown in Figure Four. The cathode "C" was notched so as to gather the metallic globules which were formed and protected them from the action of the chlorine liberated at the anode. He further prevented the metal the action of the gas on the metal by placing a thin partition between the two electrodes which also might be an electrical conductor.

Matthiessen, in 1886, did some excellent work along these lines. He found that the action of potassium chloride aided in making a better electrolyte. The work progressed

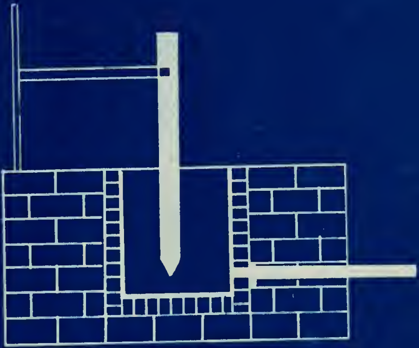

Figure 5

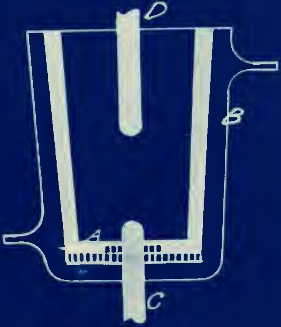

Figure 6

rather slowly until about 1881, when much experimental work was started both in United States and Germany. No work was done tending to improve the conditions of the electrolyte itself, but a study of the types of cells most advantageous for the work was taken up. Figure Five is a diagram of the cell first used by Fischer. A graphite crucible was chosen on account of its large conducting power and its resisting power to the action of chlorine gas. The anode was a vertical carbon rod. The crucible itself was the cathode. The crucible was packed tightly in magnesite brick and heated externally. It was found that the metal agglomerated on the sides of the crucible and was difficult to remove.

A new set of apparatus was designed as in Figure Six. The crucible "A" was of iron with a water jacket "B" of copper. The cathode "C" came up from the bottom and was insulated from the cell by asbestos. A carbon rod "D" coming down like an

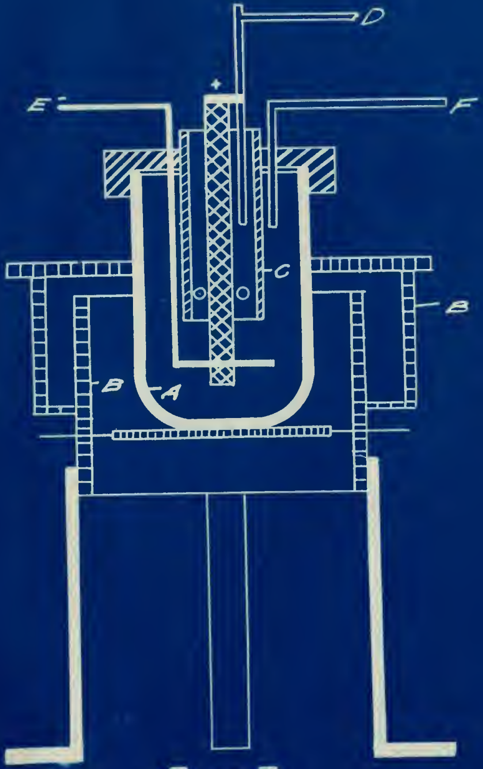

Figure 7

ard formed the anode. The metal was deposited at the cathode and stayed at the bottom of the cell where it was free from the action of the chlorine.

The cell which he ultimately decided upon is shown in Figure Seven. The crucible "A" is packed in asbestos coverings "B" so that the maximum heat will be retained in the cell. It is heated by the burner itself and is covered with an asbestos cover to shut off the air supply. A porous tube "C" perforated at the bottom was inserted so as to completely surround the anode and act as a carrier of the free chlorine to the tube "D". The wire rod "E" served as the cathode. An inert gas was introduced through "F". The inventor claims a yield of twelve grams of metal per hour using fifty amperes at ten volts as the electromotive force and keeping the electrolyte at 650°C. There is doubt in the author's mind as to the practicality of the use of nitrogen as the inert gas, since at that temperature, the

nitride of magnesium is formed.

The work was continued by Dr. Oettal who made a study of the chemical reactions taking place within the cell and his published works have been referred to in this thesis. A patent was issued to Graetzel in 1863 by the German Government, a description being found under "Bibliography" with a diagram as in Figure Two. The invention was a complete failure.

Since 1900, a large number of patents have been issued in United States to Mr. T. L. Roberts and Messrs. Seward and von Kügelchen of the Virginia Laboratories, the latter having in all about 15 patents relating to the production of metallic magnesium. Their work is mainly on the preparation of a fused electrolyte with the addition of various fluxing materials as a means of changing the specific gravity of the electrolyte.

ECONOMIC VALUE

From the standpoint of the practical man, the choice between an electro-chemical process and one that does not depend upon the application of the electrical current depends only on the relative monetary advantage of the process. The price of magnesium alone has held it to the very restricted and limited use, despite its high reducing power.

With the efficiency of the process at not more than 50%, and the relative high cost of the current necessary for the electrolysis, the choice of the metal, less effective chemically, but at the same time cheaper is desirable. This metal is aluminum and until a process can be evolved so as to be able to compete with the less valuable metal, that metal will not be used.

Magnesium is used in the dehydration of the ethers, alcohols and oils, being best suited for the work, since the magnesium hydroxide formed in the reaction is insoluble in these substances. It is also used to a limited extent in the metallurgical operations due to its high cost, in the refining of

copper, german silver, nickel and steel. Its purpose is best illustrated in this work as a reducing agent, removing the entangled oxides and reducing them, as well as removing the phosphides and sulphides. It does not remain in the finished product. Together with aluminum, it is used to make an excellent alloy, not very easily corroded. By far its greatest use is in photography and pyrotechny.

EXPERIMENTAL WORK

The Preparation of the Bath.

The crystallized magnesium chloride is melted in its own water of crystallization, potassium chloride and ammonium chloride being added to assist in the melting so that no magnesium salt is changed from the chloride to oxide condition during the fusion. The charge was as follows:

203 grams of Magnesium Chloride. ($MgCl_2$ $6H_2O$)
74 grams of Potassium Chloride. (KCl)
50 grams of Ammonium Chloride. (NH_4Cl)

From the above figures, it can be readily seen that the charge is made up of molecular proportions of the salts used. Upon fusion, 327 grams of the material will weigh 195 grams, or a loss of about 40% by weight. Analysis of the fused material shows the following composition.

$MgCl_2$	................53.14%
MgO	.... 2.69%
KCl	................43.09%
$FeCl_3$	.... 1.04%

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The bath upon first being heated will assume a very pasty consistency and then become solid again. During this period, the water content is being eliminated. It is totally impossible to drive off the entire water of crystallization at this time. According to Dr. Erich Muller, only four molecules of water of crystallization are driven off at 180°C. It is almost impossible to lose the last two molecules of water without fear of breaking up some of the magnesium chloride. It is for this reason that the potassium chloride is added. It prevents the ordinary spontaneous decomposition of the magnesium chloride and also lowers the melting point of the bath. If not added, the following reaction will take place;

$$MgCl_2 + H_2O \rightarrow MgO + 2HCl$$

The ammounium chlorids is added to break up the magnesium chloride in the bath. The reaction is as follows;

$$MgO + 2NH_4Cl \rightarrow MgCl_2 + H_2O + 2NH_3$$

If magnesium sulphate is present in the bath, it must be elimanated for it is chamged to the oxide

and will in time stop the electrolysis within the cell. It reacts as follows;

$$MgSO_4 + Mg \longrightarrow 2MgO + SO_2$$

It is best eliminated by the use of charcoal, which reduces the oxide and then can be converted by the action of the ammonium chloride.

$$MgSO_4 + C \longrightarrow MgO + CO + SO_2$$

The mass must be stirred continuously during the entire melting and fusing operation. It is poured while in the molten state upon a cold, dry and clean iron plate, allowed to cool, broken up and then stored in a bottle to exclude all moisture. All ammonium chloride is driven off before the pour since it does not assist in the electrolysis. The fused material when cold has a slight coloration, brownish in hue, due to the small iron content. It is exceedingly brittle and crystalline in body.

Preliminary Experiments.

The early experiments were conducted on a very small scale, using a porcelain crucible, five centimeters in diameter. The heat was supplied by a Meker gas burner. The anode was a 1/8" carbon rod and the cathode a thin iron wire looped at the end extending into the fused salt electrolyte so as to collect any metal which might come down in the electrolysis. In all this work, the electrical current was obtained from ten Edison storage cells, since no line could be obtained to the the proper voltage and amperage. The small amount of metal formed in the run was spongy and minute particles as globules were found with the aid of an enlarging lens.

Several experiments were conducted in a small clay pipe similar to that used by Bunsen. The carbon acted as the anode and a long wire through the stem acted as the cathode. No attempt was made to agglomerate the minute globules of magnesium.
T The work next proceeded to a thin sheet iron crucible which acted as the cathode. A 1/2" carbon

rod was the anode. The heat of the Meker burner was not sufficient to keep the material molten throughout, the the run was continued so as to get an idea as to the amount of heat necessary to carry on the electrolysis, and to see whether it could be best carried on in the semi-fluid or the molten condition.

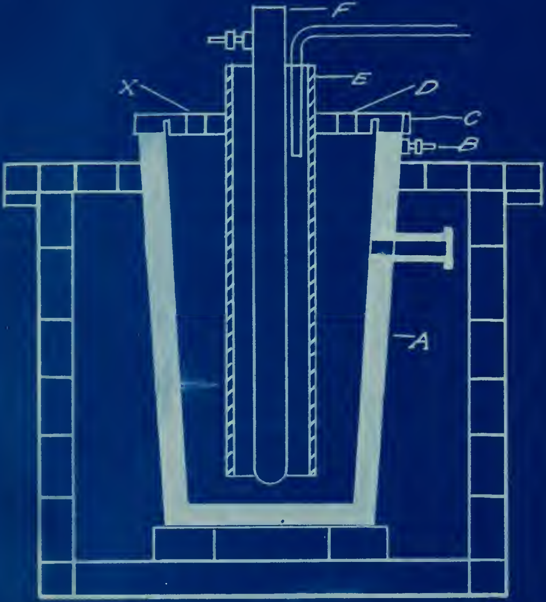

Figure 8

The Type of Cell.

The following principle was adhered to in the operation of the cell which was used in a large number of runs as is shown in Figure Eight. The crucible "A" is of cast iron and is made the cathode by the cable "B". It is covered with a thin grooved cast iron cover "C" to make the cell air-tight. An entrance pipe "D" passes through the cover and leads in the inert gas which must be free from oxygen. It passes through the cell and is led out through "X". The carbon anode "F" is contained in the tube "E" made of porcelain with a hun at the end. Through it, the hot chlorine gas liberated at the anode is led off and thus protected the metal from the gas. The crucible is filled to two-thirds of its volume with the fused salt and kept in the molten condition by external heat. The products of the electrolysis are chlorine and magnesium. The latter is deposited at the cathode and is then prevented from oxidation by the inert gas.

General Experiments.

In the next experiments, the apparatus shown in Figure Eight was used, the cell acting as the cathode and the carbon rod, 1/2" in diameter as the anode. The carbon was firmly fixed in the center of the anode compartment by means of plaster paris. A hard glass tube extended through the plaster of paris into the porcelain tube and was connected to the blower which carried off the liberated gas. The gas furnace was utilized in this work as the source of heat. Air was supplied to the furnace for mixture with the gas by a pump operated by steam in the Industrial Chemistry Laboratory and was led into the Metallurgical Laboratory where the experimental work was being carried on, by a pipe line. The record of temperature was made for all runs with the Hoskins Pyrometer. In the first run, no magnesium was found in the bath after the electrolysis, but very large amounts of magnesium carbide were present, grayish in appearance and evolving considerable acetylene.

In the next attempt to electrolysis the fused salt, the current was allowed to pass for one hour and then

fluorspar, equivalent to five per-cent by weight was added in the powdered form. The bath froze immediately and a higher temperature was required to keepthe bath in the molten condition. The current was 41.6 amperes, the voltage 7.57 and the temperature range from 700°C to 800°C. Upon opening the crucible and thus exposing it to the air for a few moments, there was a bright flame from the interior of the crucible due to the complete combustion of the magnesium which had been formed by the electrolytic action and floated with the aid of the fluxing material, fluorspar. The data on the run is given in Table One.

In the next run the conditions were the same as in the previous run, except that powdered charcoal was added as a protective layer to protect the metal formed from the oxygen and thus allow combustion to take place, even partially.
Fluorspar was added after the electrolysis had taken place, the contacts were broken and the heat raised to insure the proper flotation of the metal. The mass when broken up showed one fair sized piece of

THE PRODUCTION OF MAGNESIUM BY ELECTROLYSIS.

Table One

Charge.

525 grams of fused salt.

32 grams of fluorspar.

Time	Amperes	Volts	Temperature	
10.15	0	0	900°C	Too
10.20	45	9.55	944	High
10.25	47	8.20	760	
10.30	47.5	7.80	800	
10.35	45	7.50	680	
10.40	43.5	7.30	740	
10.45	41	7.50	780	
10.50	40	7.40	780	
10.55	40.5	7.15	740	
11.00	39	7.10	760	
11.05	38	6.95	760	
11.10	37	6.80	770	
11.15	36	6.75	780	

metal which had a layer of oxide on it. About fifteen grams of the carbide was formed and was very active in water. The layer of oxide on the metal was rather heavy and it took the full heat of a Bunsen burner to ignite it. At the start, the fused salt had a light brown coloration due to the iron contamination, and after the electrolysis had taken place and the salt poured out, the mass was grayish in appearance and its structure was in the form of long needle shaped crystals. There were no special reasons for this and the author is unable to account for this, even though it did not occur in any of the other experiments. The data obtained on this run is tabulated in Table Two.

A run was made using the iron crucible as the anode and the carbon rod as the cathode, the idea being to have the porcelain tube act as the surrounding medium for any magnesium that would be formed at the carbon cathode, while the gas which was formed would escape through the two

THE PRODUCTION OF MAGNESIUM BY ELECTROLYSIS.

Table Two

Charge.

195 grams of fused salt.

12 grams of fluorspar.

Time	Amperes	Volts	Temperature
12.00	0	0	680°C
12.05	39	8	Constant
12.10	40	7.5	
12.15	40	7.00	
12.20	40.25	6.80	
12.25	38	6.60	
12.30	32.50	6.60	
12.35	32	6.40	
12.40	31.50	6.30	
12.45	31.	6.20	
12.50	29.50	6.10	
12.55	27.55	6.00	
1.00	27.50	6.00	
1.05	25	6.00	

Yield .244 grams of Magnesium Metal

15 grams of Magnesium Carbide

holes in the cover, one of which was used for the pyrometer and the other as a feed hole. No results were obtained, the carbon rod being well eaten up and the crucible so corroded by the gas that it had to be discarded.

A run was then made using the regular charge with the addition of ten per-cent of barium chloride. Patents had been issued to Seward and Kugelchen who claimed that this salt, on account of its extreme heaviness would float the metallic magnesium formed in the electrolysis of the fused salt. A run of ninety minutes was made, and no metallic magnesium, not even in the small globular form were found. However, the author found that the experiment could be carried on at a much lower temperature with the addition of the barium chloride. Conditions began to vary so greatly after the run had proceeded for one hour that the author came to the conclusion that the resistance of the electrolyte had become so great as to cause the Edison cells to discharge so rapidly as to injure them. The run was discontinued shortly afterwards. The data is given in Table Three.

THE PRODUCTION OF MAGNESIUM BY ELECTROLYSIS.

Table Three

Charge.

300 grams of fused salt

30 grams of barium chloride.

Time	Amperes	Volts	Temperature
11.00	0	0	640°C
11.05	17	9.7	
11.10	21	9.0	
11.15	24.5	8.2	600
11.20	23.5	8.0	680
11.25	23.5	7.9	640
11.30	24	7.5	660
11.35	22.5	7.6	640
11.40	22.5	7.5	600
11.45	23	7.1	
11.50	22.5	7.1	
11.55	22	6.8	
12.00	21.5	6.5	660
12.05	25	6.3	
12.10	22	5.4	
12.15	15	4.8	
12.20	14	4.7	
12.25	14	4.7	
12.30	17.5	4.5	600°C

No metal was found.

THE PRODUCTION OF MAGNESIUM BY ELECTROLYSIS.

Discussion.

The cause of the failure of the metal to agglomerate is due to the fact that a thin layer of magnesium oxide had coated the metallic globules, thus preventing them from coming together into mutual contact. This by itself, is not convincing enough, however, since it might be supposed that the oxide would dissolve in the carnallite and finally be reduced to the chloride. Calcium fluoride did not aid materially in the removal of the oxide film as has been claimed by many authors. It does not decrease the temperature of fusion, but does raise the specific gravity of the bath and in that way allows the globules to float.

In this thesis, the author has attempted to replace the inert gas by a solid material, which would not allow the combustion of the metal at the temperature of electrolysis. Powdered charcoal was used throughout the work with the same degree of effiviency as the inert gas. It is the

reducing medium. It acted admirably in this respect. There is a slight possibility that t at a much higher temperature than this work is being carried on at, that there might be a recation between the metal and the reducing agent.

The electrolyte when poured and in the solid state, showed dark brown and black spots. These spots were cut out and examined. There structure was decidedly different from that of the magnesium carbide which was always present as a product of the electrolysis. One of these spots was placed in a test tube and cold distilled water was added. There was a weak reaction between the water andn the substance underrsurveilance. The small amount of iron present as a salt colored the solution light brown. When the whole mass had dissolved, and the gas reaction had taken place, a very small globule of magnesium was found at the bottom of the test tube. Another piece was placed in a porcelain crucible and heated with a blast burner, the cover being placed on the crucible and hydrogen being

supplied through a small opening in the cover. The metal itself could not be freed from the material in this manner, nor could it be reduced. The author has come to the conclusion that the electrolyzed material, when poured, contains some metal at a temperature too low for ignition, but still active enough to combine to a certain extent with oxygen in the air to give a film of oxide as a coating. Magnesium oxide is white and since these spots were dark, the author concludes after the works of others have been read on this same point, that a true sub-oxide is formed and that this is a hindrance to the successful electrolysis of the fused salts.

The author has also found that the crucible setting in the furnace must be a fixed condition in the run, or the furnace will tend to corrode the metal . If the crucible is placed in the furnace in the absence of a reducing gas, even though powdered charcoal is used, the walls will suffer from excessive corrosion above the level

of the fused material.. This can be readily accounted for by stating that the metallic crucible was being chloridized and that the furnacesgases and the acid within the cell had an action on it tending to corrode it.

THE PRODUCTION OF MAGNESIUM BY ELECTROLYSIS.

Summary.

Metallic magnesium can be obtained by the action of the electric current on the fused magnesium chloride. The bath must be carefully prepared so as to be free from traces of magnesium oxide which seems to hinder the electrolysis, since it forms a film around the globules as fast as they are formed at the cell. The globules are unable to come together on account of the film which seems to check the metal from coming in mutual contact with the other particles.

The temperature at which the process should be carried on should be between 650°C and 750°C. Between this range, the bath will be a thickly fused electrolyte and a liquid and molten bath at a low red heat.

The voltage should be not less than five volts, which is near enough to its decomposition voltage for the work. The current for this work should be a constant one and the fall of potential should

not be great. For this reason, the author suggests the use of a motor generator rather than a set of storage cells which has been used in this work.

The author does not believe that the iron cell which he has used in this work is wholly adapted for the work, though by far it is the cheapest nor does he believe that they can resist the furnace gases without much loss due to oxidation which will in time make the cell useless. A graphite or carbon crucible will not serve if the heat is furnished by the furnace, but if it is heated by resistance, it should serve well.

No study has been made of the conditions for the removal of the metallic magnesium. The author does believe however, that if a cell is designed and chosen as to meet with the following requirements for the work, namely,

1. To be a good electrical conductor.

2. To withstand the action of the furnace

gases without being acted upon.

3. To withstand the corrosion due to the action of the electrolyte as well as the gas which is formed.

the metal can be successfully formed and floated by raising the specific gravity of the bath and then adding more of the fused salt to that of a pipe branching off horizontally from the cell itself and leading into an atmosphere of hydrogen. Or, after the electrolytic action has taken place, the bath can be cooled slowly until it begins to thicken and then poured into a receptacle and pulverized so that the metal can be taken out. The former method is by far the more preferable, since it is more technical.